UTILIZATION OF WASTE

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USE OF METALLURGICAL SLAG FOR AVENTURINE GLASS SYNTHESIS

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Glass with an aventurine effect in the lead-boron-silicate system has been developed using metallurgical slag. The experimental results are processed based on probability theory and random process methods. A mathematical model of the charge is developed. The role of the slag in the process of glass synthesis is determined.

The methods and procedures of glass technology make it possible to obtain materials that are close in their outward appearance and internal structure to natural minerals. This is one of the most significant features that makes glass products indispensable in the production of decorative materials.

The present paper describes the investigation of glass with an aventurine effect in the lead-boron-silicate system using metallurgical slag (patent RF 2035415). Slag is an industrial waste from processing of iron into steel. It is an amorphous glass-like substance. The basic chemical components are iron, chromium, silicon, calcium, and sodium.

For the sake of more convenient interpretation of the experimental data, the components of the charge were divided into three groups: glass forming, crystal forming, and alkaline components. Slag as a charge component was included in the crystal forming group.

The charge was founded in a crucible in an electric furnace at a temperature no higher than 1100°C (SNOL-1.6.2,5.1/11-M1 U4.2 furnace, maximum heating up to 1100°C). After annealing of the glass, the degree of the scintillation effect was assessed visually and with the Biolam optical microscope, and the predominant crystal size was appraised. Processing and analysis of the experimental results were carried out using probability theory and random process theory [1].

Fig. 1 shows photos of the glass samples made in reflected light using a NEOPHOT-32 optical microscope. It can be seen that two crystal phases were formed: a trigonal phase of the hematite type and a pseudohexagonal one of the mica type.

The crystals are flat and lamellar. Extremely fine (4 – 5 μm) as well as very large (up to 900 – 1000 μm) crystals were formed (Fig. 1*a*). The hexagonal crystals differed from the trigonal ones in their optical density; the former are more transparent, and the underlying crystals are clearly seen through them. The optical density of the trigonal crystals is greater, and the structure of the underlying layers cannot be seen through them. The hexagonal crystals seem to be extremely thin since a moire pattern is clearly visible.

Special interest was elicited by the optical pattern typical only of pseudohexagonal crystals and not observed in trigonal ones. This pattern consists in a series of alternating light and dark contours of varying brightness. The contour lines that are nearer to the edges are sharper and thinner, as distinct from the ones located closer to the center, which are broader, and their color transitions are more blurred. This optical effect is related to the nature of the distribution of stresses arising in the course of crystal growth, their spatial arrangement and different width. Fig. 1*b* clearly reveals the process of layer-by-layer growth of hexagonal crystals, and Fig. 1*d* represents the stages of development of trigonal crystals. Along with the contrasting patterns, all photos show less clear contours of the crystals submerged in the vitreous mass of the matrix.

In the course of the experiment, 29 foundings were carried out. The charge compositions are shown in Fig. 2 and 3. For convenience of mathematical processing, the results obtained are presented in logarithmic form.

The field in Fig. 2 is divided by vertical lines into 4 sites according to the histogram shown in the upper part of the figure. The histogram is constructed according to the crystal sizes observed in the glass samples:

Site I — no crystals were observed;

Site 2 — crystal size 5 – 50 μm, individual crystals up to 100 μm;

Site 3 — crystal size 5 – 100 μm, individual crystals up to 300 μm;

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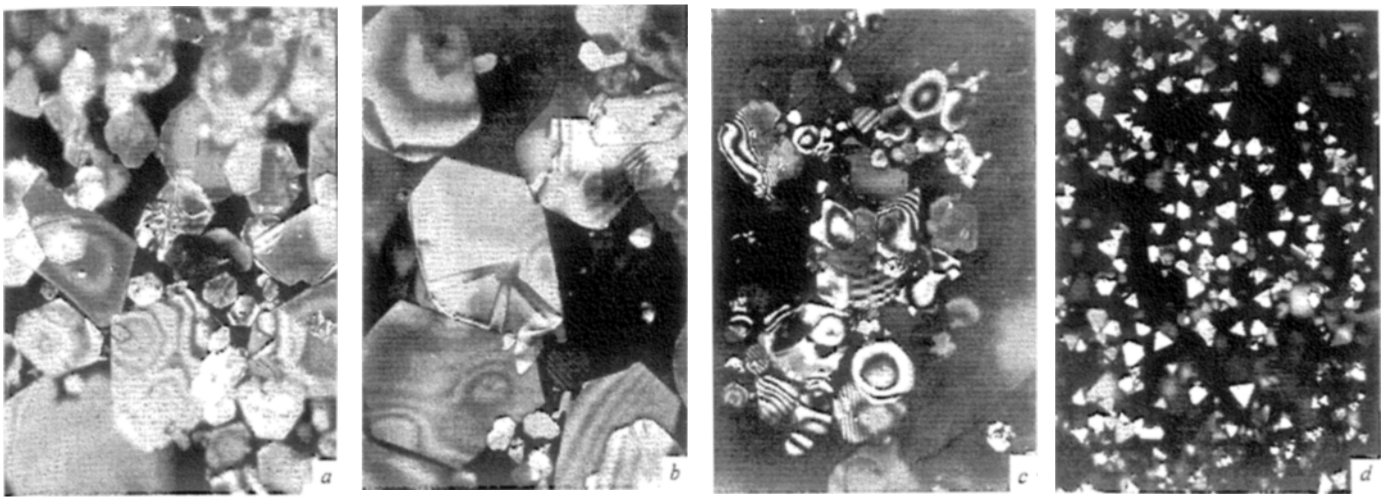

Fig. 1. Crystalline phases of aventurine glass: *a*) × 500; *b*) × 800; *c*) × 400; *d*) × 1000.

Site 4 — crystal size 5 – 500 μm, individual crystals up to 1000 μm.

The scintillation effect was exhibited most clearly in the glass samples obtained from charges 23 – 29.

It was established that with a content of crystal-forming components in the charge above 38%, the probability of complete loss of the scintillation effect is high. An increase in the content of alkaline components also produced decreased manifestation of this effect and, finally, its complete loss. Besides, corrosion of the crucibles was accelerated. The area of a high content of glass-forming components was not studied due to the limited capabilities of the furnace.

Taking into account the peculiarities of charges 23 – 29, correlation regression analysis and approximation of the curves were made.

Approximation of curves GF, CF and AC on site IV was performed with exponential functions of the general form

$$X_{i\,\mathrm{AC}} = A\exp(B),$$

where X is the concentration of the respective charge component; i is the number of the experiment; A is the exponential factor; B is an exponent.

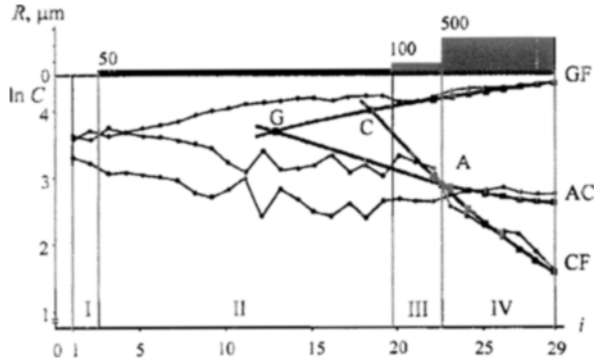

Fig. 2. Changes in the content of the charge components ln C and histogram of the change in size R in the glass: i) charge number; GF) glass-forming components; CF) crystal-forming components; AC) alkaline components.

The problem was to determine the values of the exponential factor and the exponent.

The meaning of factor A consists in the fact that theoretically it represents the maximum possible content of the charge component, i.e., 100%. In this case the sign of the exponent of number A in the case of a monotonical increasing curve GF is positive, and for the monotonical decreasing curves CF and AC, it is negative. The signs of exponent B were distributed in a similar way.

Since the area of the compositions between site III and site IV is transitional, the component contents in charge 22 were taken as the first change limits, and the content of glass-forming, crystal-forming, and alkaline components in charge 29 were taken as the second limits. The approximation results of the experimental curves in the area of the best aventurine effect are given in Table 1.

Setting the values of the exponent from the intervals established, the points of the approximation curves were calculated. In Fig. 2 they have the appearance of smoothly changing lines. The points of mutual intersection of the approximating curves (points G, C, A) were determined. These points delimited the area of the charge compositions inside the concentration triangle (Fig. 3) in which the probability of

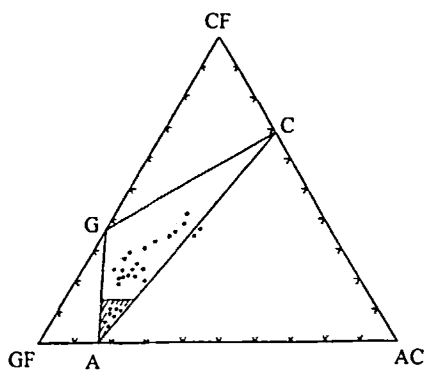

Fig. 3. Concentration triangle of charge compositions.

TABLE 1

Approximating curve on site IV	Approximating function	Change limits of the exponent
GF	$X_{iGF} = 4.6052 \exp(B_{GF})$	$-0.1 < B_{GF} \le -0.05$
CF	$X_{iCF} = 0.2171 \exp(-B_{CF})$	$-2.55 < B_{CF} \le -2.00$
AC	$X_{iAC} = 0.2171 \exp(-B_{AC})$	$-2.56 < B_{AC} \le -2.48$

TABLE 2

Charge components	Parities correlation coefficient ρ	Regression coefficient β	Regression functions $G(X_i)$
CF–GF		7.98	$G_{CF}(X_{iGF}) = 7.98X_{iGF} + 36.61$
GF–CF	0.89	0.10	$G_{GF}(X_{iCF}) = 0.10X_{iCF} + 4.53$
CF–AC		0.93	$G_{CF}(X_{iAC}) = 0.93X_{iAC} + 4.69$
AC–CF	0.25	0.01	$G_{AC}(X_{iCF}) = 0.01X_{iCF} + 2.79$
CF–AC		0.24	$G_{GF}(X_{iAC}) = 0.24X_{iAC} + 4.99$
AC–CF	0.11	0.26	$G_{AC}(X_{iGF}) = 0.26X_{iGF} + 3.89$

obtaining glass with an aventurine effect is high: the glass-forming content (point G) — 63.3%, content of crystal-forming component (point C) — 68.8%, content of alkali in the charge (point A) — 15.8%.

Having performed geometrical constructions inside triangle GCA, the area of the most promising charge compositions for obtaining glass with the best decorative effect was singled out (shaded). Point A should be excluded from consideration: in this point the triple system degenerated into a double system. The control foundings of the charge confirmed the validity of this conclusion.

The results of the correlation-regression analysis of the experimental data (compositions 23 – 29) are given in Table 2.

All components of the charge chosen for obtaining glass with the best aventurine effect were interrelated. In the group CF–GF (GF–CO), the dependence is most significant ($\rho = 89\%$). In all probability, slag, as a crystal-forming component, is at the same time a glass-forming component. ($\rho_{CF\text{-}GF} = 7.98$) and accelerator of batch founding. ($\beta_{CF\text{-}AC} = 0.93$) Slag is a crystal forming component, and neither glass former, nor alkali former could adopt this function (low values of ρ and β). It was established that the slag was acting as a tinting colorant.

In the course of the experiment, in principle glass could be obtained without additional introduction of alkalis but in the case considered they were necessary as accelerators of charge founding $\rho_{GF\text{-}AC(AC\text{-}GF)} = 11\%$. With respect to the crystal-forming components, the alkaline components also act as fluxes. This is because the relationship CF–AC (AC–CF) is correlated by 25%, i.e., the glass-forming components and alkalis were the environment for forming crystals.

Taking into account the exponential functions with their limiting conditions, the prevailing crystal sizes in the glass with the best aventurine effects, temperature limitation of founding, correlation coefficients and regression functions, mathematical model of the charge was represented in the following form:

$1000°C < t < 1100°C$

$R \approx 500\ \mu m$

$X_{iGF} = 4.6052 \exp(B_{GF}),\quad -0.1 < B_{GF} \le -0.05;$

$X_{iCF} = 0.2171 \exp(-B_{CF}),\quad -2.55 < B_{CF} \le -2.00;$

$X_{iAC} = 0.2171 \exp(-B_{AC}),\quad -2.56 < B_{AC} \le -2.48;$

$$\rho_{CF\text{-}GF(GF\text{-}CF)} = 0.89:\quad G_{CF}(X_{iGF}) = 7.98X_{iGF} + 36.61;\quad G_{GF}(X_{iCF}) = 0.10X_{iCF} + 4.53;$$

$$\rho_{CF\text{-}AC(AC\text{-}CF)} = 0.25:\quad G_{CF}(X_{iAC}) = 0.93X_{iAC} + 4.69;\quad G_{AC}(X_{iCF}) = 0.01X_{iCF} + 2.79;$$

$$\rho_{GF\text{-}AC(AC\text{-}GF)} = 0.11:\quad G_{GF}(X_{iAC}) = 0.24X_{iAC} + 4.99;\quad G_{AC}(X_{iGF}) = 0.26X_{iGF} + 3.89.$$

Thus, decorative glass with an aventurine effect in the lead-boron-silicate system with the use of metallurgical slag was developed. The glass can be used in the construction, furniture-making, jewelry and other sectors of industry.

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REFERENCES

1. G. Corn and N. Corn, *Mathematics Manual for Researchers and Engineers* [Russian translation], Nauka, Moscow (1973).